Test Material: Dicamba

MRID: 49937701

Title: Sampling for Possible Gaseous Field Loss after Application of a Commercial Herbicide

EPA PC Code: 100094

OCSPP Guideline: 835.8100

For CDM/CSS-Dynamac JV

Primary Reviewer: Richard Lester   **Signature:**

Date: 10/5/16

Secondary Reviewer: Kathleen Ferguson   **Signature:**

Date: 10/5/16

QC/QA Manager: Joan Gaidos   **Signature:**

Date: 10/5/16

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel.

Field Volatility of Dicamba

Report:	MRID 49937701. Jackson, S.H. 2016. Sampling for Possible Gaseous Field Loss after Application of a Commercial Herbicide. Unpublished study. Study performed, sponsored and submitted by BASF Crop Protection, Research Triangle Park, North Carolina. Study No.: 813945; BASF Registration Document No.: 2016/7005721. Study initiated March 9, 2016, and completed May 6, 2016 (p. 8). Final report issued June 1, 2016.
Document No.:	MRID 49937701
Guideline:	OCSPP 835.8100
Statements:	This study was conducted according to the USEPA FIFRA Good Laboratory Practice (GLP) Standards (40 CFR Part 160), with the following exceptions (p. 3):

1)   The test substance used in the field phase of this study was a commercial product obtained from commercial production. The lot numbers for each were obtained, but the individual test substances were not characterized as required under GLP or archived.

2)   The Exponent modeling report appended to this study is an evaluation of data after generation and was not conducted under GLP.

Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).

Classification:	This study is Supplemental. The estimated flux values are not calculated correctly. Application verification samples contained only 67% and 77% of the targeted applied amount of dicamba at Sites 1W and 2E, respectively. Reviewer calculated meteorological parameters do not agree with reported values. The soil matrix was not sampled. Estimated flux values with the indirect method are limited by few detects above the LOQ. The minimum fetch required for use of the aerodynamic method was not satisfied for all samplers. The initial air monitoring period did not start at the beginning of the application period, but instead started immediately following the application period. An independent laboratory method validation was not conducted.
PC Code:	100094
Reviewer:	William P. Eckel, Ph.D. **Signature:** _William P. Eckel_
	Date: January 12, 2017

Executive Summary

Field volatilization of dicamba, formulation Engenia®, a formulation containing 5 lb. a.e./gal, was examined from two cropped plots in Sumter County, Georgia. The sites where the studies were conducted were near Plains, Georgia. The experiments at these sites (Sites 1W and 2E) were conducted for approximately two days. The nominal application rate in the plot was 1 lb.

a.e./A. The treated plots were approximately 1.75 km apart. This plot was approximately 1000 ft generally downwind from a plot for another study conducted on the same days. No control plot was used, but untreated control sampling locations were located 52 m south of Site 1W and 75 m southwest of Site 2E.

Under field conditions at Site 1W, based on calculations using the Aerodynamic method, a peak volatile flux rate of 0.0022 µg/m^2·s was measured accounting for 0.021%[1] of the applied observed 3 to 6 hours post-application. By the end of the study, a total of 0.060% of the applied dicamba volatilized and was lost from the field. No secondary peak volatile flux rates were observed.

Under field conditions at Site 1W, based on calculations using the Indirect method, a peak volatile flux rate of 0.011 µg/m^2·s was measured accounting for 0.11% of the applied observed 3 to 6 hours post-application. By the end of the study, a total of 0.21% of the applied dicamba volatilized and was lost from the field. No secondary peak volatile flux rates were observed.

Under field conditions at Site 2E, based on calculations using the Aerodynamic method, a peak volatile flux rate of 0.0014 µg/m^2·s was measured accounting for 0.014% of the applied observed 0 to 3 hours post-application. By the end of the study, a total of 0.038% of the applied dicamba volatilized and was lost from the field. No secondary peak volatile flux rates were observed.

Under field conditions at Site 2E, based on calculations using the Indirect method, a volatile flux rate of 0.00099 µg/m^2·s was measured accounting for 0.015% of the applied observed 6 to 12 hours post-application. Only a single volatile flux rate was estimated due to the observation of only a single detect at offsite monitors.

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[1] All percentages of the amount applied are reviewer calculated based on the application rate and flux rates presented in MRID 49937701.

Figure 1. Dicamba Flux Rates for Site 1W
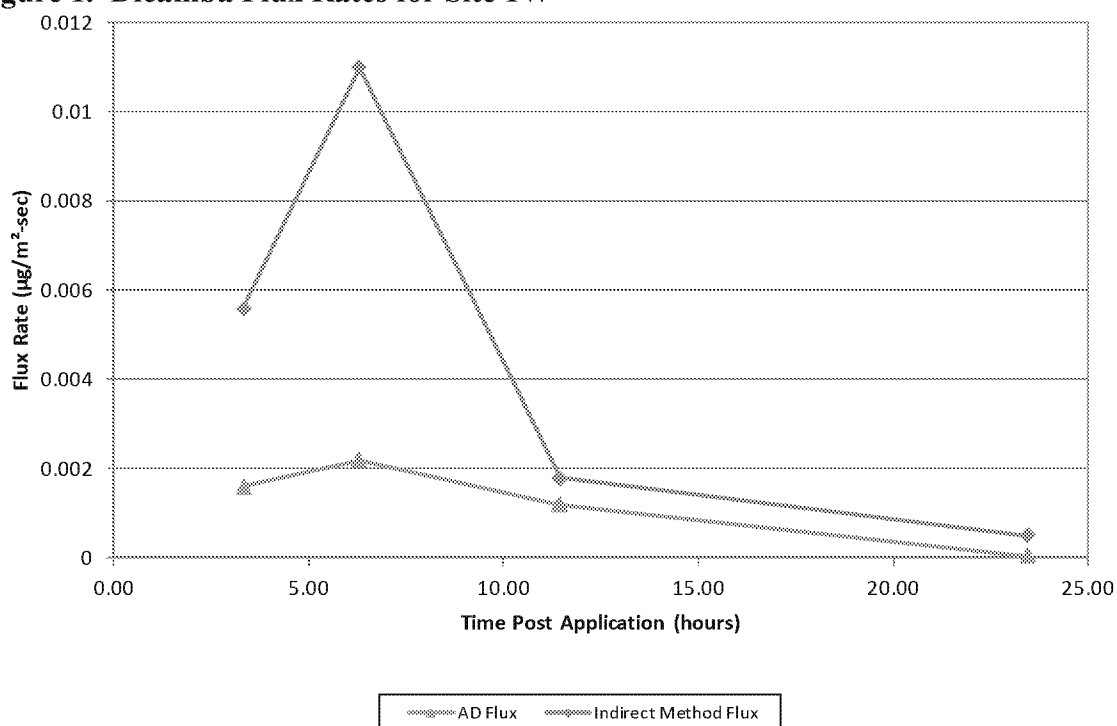
Figure 2. Dicamba Flux Rates for Site 2E
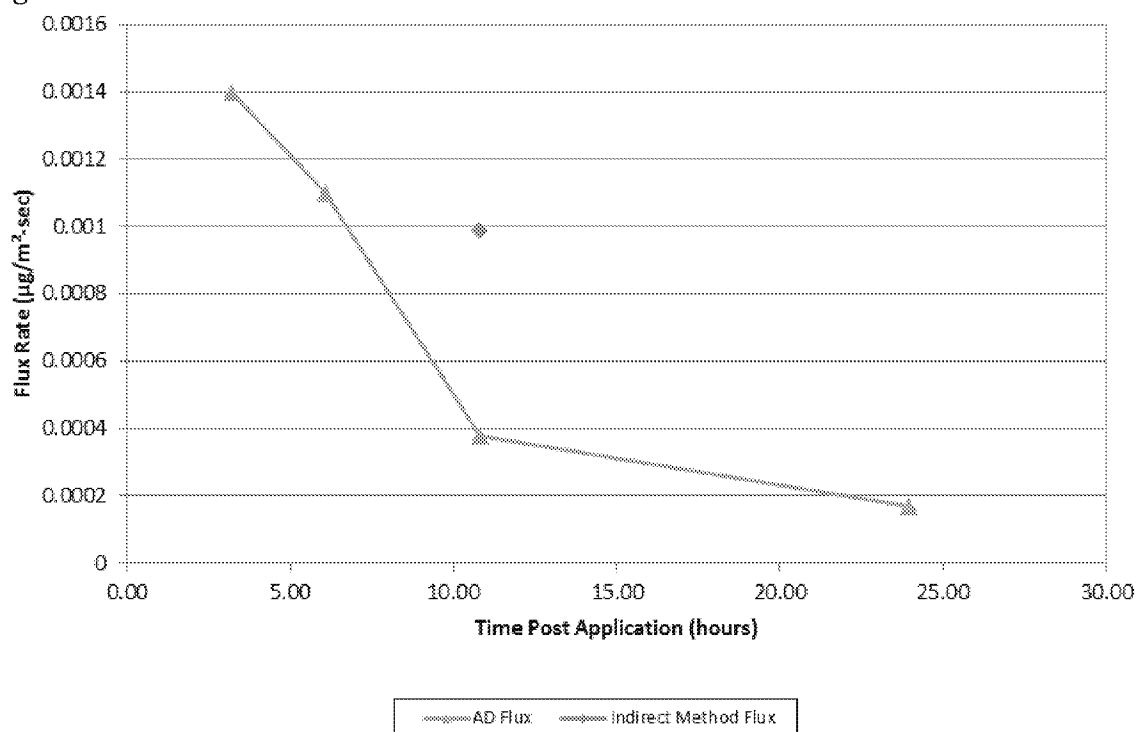
I. Materials and Methods

A. Materials

1. Test Material

Product Name: Engenia® (p. 11)
Formulation Type: Not reported.
CAS #: 104040-79-1 (dicamba BAPMA salt)
Storage stability: Not reported.
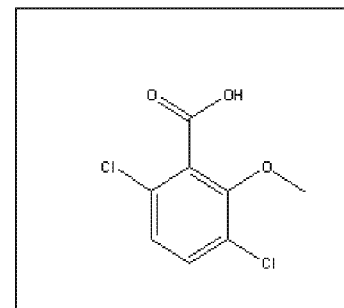
2. Storage Conditions

The test substance was stored at ambient temperature (17.9°C to 22.9 °C) prior to the application (p. 32).

B. Study Design

1. Site Description

The test sites were located approximately 3 km northwest of Plains, Sumter County, Georgia (pp. 32-33) and were separated in distance by about 1.75 km (p. 11). The treated area at each test plot was approximately 120 m × 120 m. The test sites were uniform with respect to soil texture and vegetation and near uniform regarding slope with natural undulation present between 2% and 5%. Agronomic and pesticide use history of both plots was documented for three years preceding the study (pp. 34-35; Table 1, p. 39).

The test plot at Site 1W was located within a rectangular agricultural hay field measuring approximately 220 m × 440 m with a gradual diminishing slope from north to south (p. 33). The crop was mixed species hay dominated by Bermuda grass (*Cynodon* spp.) and Orchardgrass (*Dactylis* spp.) that was mowed to a height of six to eight inches prior to application. The USDA taxonomic soil classification for the field is Norfolk loamy sand (p. 12).

The test plot at Site 2E was located within a trapezoidal agricultural hay field measuring 145 m wide at the north end, 265 m wide at the south end, 350 m long at the west end, and 290 m long at the east end (p. 33). The crop was mixed species hay dominated by Bermuda grass (*Cynodon* spp.) and Orchardgrass (*Dactylis* spp.) with a height of 15 to 18 inches. The USDA taxonomic soil classification for the field is Orangeburg loamy sand (p. 12).

2. Application Details

Application rate(s):   The target application rate was 1.0 lb a.i./A (p. 14). Based on swath pass times, swath distance, and the calibrated sprayer flow rate, the actual application rate was 1.03 lbs a.i./A for Site 1W and 0.97 lbs a.i./A for Site 2E (Table 2, p. 14). Application verification

samples contained 67% and 77% of the target dicamba at Sites 1W and 2E, respectively (Table 16, p. 153).[2]

Irrigation and Water Seal(s): No irrigation water was used.

Tarp Applications: Tarps were not used.

Application Equipment: The applications were made with a tractor mounted hydraulic boom sprayer equipped with a 200-gallon tank and 24-foot boom (p. 35). The boom contained 17 nozzles spaced 18 inches apart, producing an effective spray swatch of 25.5 feet. Turbo TeeJet Induction (TTI) 11005 nozzles were used per test substance label specifications. A pressure of 40 psi was selected based on manufacturer recommendations.

Equipment Calibration
Procedures: Sprayer calibration was performed by testing each nozzle and measuring the rate that liquid collected in a 2.5-gallon bucket (pp. 35-36). Verification was conducted by spraying at 40 psi for 30 seconds. Nozzles were each tested three times to determine variability between nozzles and replication. The sprayer calibration established the output to be 6.9-GPM. Using the measured volume per minute output of the boom at 40 psi and a calibrated sprayer vehicle speed of approximately 5.6 mph in first gear, a spray rate of 24-GPA was achieved and set as the target spray rate.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**.

Table 1. Summary of application methods and rates for dicamba

Site	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied* (lbs)	Area Treated (acres)	Target Application Rate (lb ae/acre)	Reported Application Rate (lb ae/acre)
1W	Tractor-mounted broadcast spray	4/11/2016 09:19	3.67	3.56	1.0	1.03
2E	Tractor-mounted broadcast spray	4/11/2016 10:23	3.45	3.56	1.0	0.97

Data obtained from p. 36 and Table 3, p. 40.
*The amount of dicamba applied is reviewer calculated based on the treated area and reported application rates for each site.

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

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[2] Reviewer calculated. Application verification samples consisting of 15 composited petri dish samples (p. 134) contained 20,013 µg dicamba/sample and 22,825 µg dicamba/sample, respectively (Table 16, p. 153). Expected dicamba per composite sample was 15 petri dishes × 1983.3 µg/petri sample = 29,750 µg dicamba/sample.

Table 2. Summary of dicamba application and monitoring schedule

Site	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
1W	3.56	04/11/16 between 09:19 – 09:32	04/11/16 between 09:32 – 12:51	Not Applicable	Not Applicable
2E	3.56	04/11/16 between 10:23 – 10:35	04/11/16 between 10:35 – 13:46	Not Applicable	Not Applicable

Data obtained from p. 36; Table3, p. 40; and Table 6, p. 41.

3. Soil Properties

The soil matrix was not sampled in the study (pp. 12, 31). Known soil properties are provided in **Table 3**.

Table 3. Summary of soil properties for fields/plots

Site	Sampling Depth	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm³)	Soil Composition
1W	NA	NA	Norfolk loamy sand	NA	NA	NA
2E	NA	NA	Orangeburg loamy sand	NA	NA	NA

Data obtained from pp. 12, 31. NA indicates not applicable because the soil matrix was not sampled.

Soil temperature and soil moisture were not measured.

4. Meteorological Sampling

Wind speed, wind direction, temperature, and relative humidity were recorded at the test sites using on-site weather stations (pp. 13, 35). Weather parameters were measured at three heights above the vegetation (approximately 0.5 m, 1.0 m, and 1.5 m above the top of the vegetation). The weather station at Site 2E was additionally equipped with a pyranometer for measuring solar radiation. On April 11, 2016, a tipping bucket rain gauge was added to the weather stations at both sites at 1.0 m above the top of vegetation due to forecast precipitation throughout the evening. Weather station data were collected and stored on a 1-minute interval at both sites for the duration of the study.

One-minute weather data are included in an Appendix to the Final Field Phase Report (pp. 50-117).

The weather stations were deployed 15 m east of the plots near sampling station D prior to application and were then moved near the center of the plot (15 m east of sampling station I) immediately following application (p. 12).

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in Table 4. The location of the meteorological equipment for the plot is shown in Attachment 3.

Table 4. Summary of meteorological parameters measured in the field

Site	Minimum Fetch* (m)	Parameter	Monitoring heights (m)	Averaging Period
1W	63.8	Wind speed/Wind direction	0.5 m, 1.0 m, 1.5	1 minute
		Ambient air temperature	0.5 m, 1.0 m, 1.5	1 minute
		Relative humidity	0.5 m, 1.0 m, 1.5	1 minute
		Precipitation	1.0 m	1 minute
2E	63.4	Wind speed/Wind direction	0.5 m, 1.0 m, 1.5	1 minute
		Ambient air temperature	0.5 m, 1.0 m, 1.5	1 minute
		Relative humidity	0.5 m, 1.0 m, 1.5	1 minute
		Precipitation	1.0 m	1 minute
		Solar radiation	Not specified	1 minute

Data obtained from pp. 13, 35; and the Appendix to the Final Field Phase Report (pp. 50-117).
* Not reported in the MRID. Value indicated is the minimum average fetch for a sampling period. Values on a per minute basis are calculated in the accompanying spreadsheets.

5. Air Sampling

Ten PVC sampling masts were constructed for each test plot to hold active air sampler pumps and PUF/XAS tube sampling media (pp. 12-14, 33-34; Figures 1-5, pp. 42-46). Nine perimeter sampling locations were set up 15 m from the plot at the corners and mid-point of each side of the plot with sample tubes suspended at a height of 1.0 m above the hay. For the central plot sampling location, a modified sampling mast with five active air samplers and tubes was set up so that sampling occurred at heights of 0.2 m, 0.4 m, 0.6 m, 0.8 m, and 1.0 m above the hay. Untreated control sampling locations were set up 52 m south of the southeast corner of the treated area at Site 1W and 75 m southwest of the southwest corner of the treated area at Site 2E (p. 33). No pre-application samples were collected.

6. Sample Handling and Storage Stability

Samples were placed into coolers with freezer packs at the test sites for temporary storage before being transferred to secure freezers at the field test facility, Harris Farms and Research (p. 37). Untreated control samples were handled and stored separately from other samples. Following experimental termination, all PUF/XAD samples were packed in coolers with blue ice and driven from the field test facility to the analytical laboratory by the Principal Field Investigator (p. 37-38). All samples were checked into freezers at the analytical laboratory at 10:26 p.m. EDT on April 13, 2016. BASF has data which indicate the stability of dicamba residues on the involved matrix for more than 5 months (p. 19). The air sampling devices were stored frozen for no more than 17 days from collection to extraction for analysis (p. 19; Tables B.1-B.2, pp. 159-170). No corrections were made to account for instability.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Dicamba was monitored using PUF/XAD sample tubes (XAD-2 OVS quartz fiber 270/140 mg sorbent tubes, SKC Inc. Catalog No. 226-58A; p. 34) and SKC Leland Legacy® active air sampler pumps (SKC Inc. Catalog No. 100-3002). Plastic polytetrafluoroethylene (PTFE) tubing was used to connect pumps to samplers. The air pumps were set to draw 3 L per minute for the designated sampling periods (pp. 17, 218).

- Extraction method: A 10-ml portion of methanol/water (90:10, v/v) acidified with 1% formic acid was added to the OVS tube. Dicamba was extracted from the sorbent by mechanical shaking for 60 minutes at 200 or 300 rpm. The sample was removed from the shaker and allowed to settle for 2-5 minutes. A 1-mL aliquot was transferred to a clean culture tube and diluted with 3-mL of 1% formic acid in HPLC water. The sample was mixed by vortexing for about 10 seconds to dissolve any dicamba residue and then vialed for analysis by LC-MS/MS (p. 130; Figure C.1, p. 173).

- Method validation (Including LOD and LOQ): Method ADPEN M1407 "Technical Procedure: Analytical Method for the Determination of Residues of BAS 183 H (Dicamba) and Imazethapyr in OVS tubes with XAD-2 sorbent by LC-MS/MS" was used to analyze OVS tube samples (pp. 14, 123). The LOQ was 0.01 µg dicamba per sample, and the LOD was 0.001 µg per sample. This corresponds to an LOQ and LOD of 0.02 µg/m^3 and 0.002 µg/m^3, respectively, for a 3-hour sampling period and an LOQ and LOD of 0.005 µg/m^3 and 0.0005 µg/m^3 for a 12-hour sampling period (p. 219). No method validation activities are specified.

- Instrument performance: The performance of the instrument was evaluated during each injection set (pp. 130-131). The correlation coefficient for each calibration curve was no less than 0.99. Calibration standard concentrations for dicamba ranged from 0.025 to 10 ng/mL. Calibration curves were linear with 1/x weighting (pp. 130-131; Figure C.3, p. 175).

8. Quality Control for Air Sampling

Lab Recovery: Most laboratory spike recoveries are within the acceptable range of 90-110% following fortification at 0.01 (13 samples), 0.1 (10 samples), 0.3 (1 sample), and 1.0 µg/sample (2 samples) (Table 1, p. 138); however, 12 of 26 recoveries were outside the acceptable range. Overall recoveries were between 77% and 111% with an average percent recovery (±RSD) of 91 ± 8.6%. The exceptions include 7 of 13 samples at the fortification level of 0.01 µg/sample, 3 of 10 samples at 0.1 µg/sample, the one sample at 0.3 µg/sample, and 1 or 2 samples at 1.0 µg/sample.

Field blanks: There was no dicamba measured in all untreated control samples collected from the two sites (Tables 3-14, pp. 140-151).

Field Recovery: No field recovery is reported.

Travel Recovery: Mean recoveries of dicamba from five transit stability samples from each
                    site fortified at 0.3 µg/sample were 88% at Site 1W (range from 86 to
                    92%) and 85% at Site 2E (range from 81 to 87%) (Table 15, p. 152).

Breakthrough: No explicit discussion of breakthrough is provided. Transit stability
                    samples fortified at 0.3 µg/sample had an average recovery of 86.5%
                    (Table 15, p. 152). The highest dicamba amount measured on a sample
                    during the study was 0.066 µg/sample (Tables 3-14, pp. 140-151),
                    indicating that dicamba loss due to breakthrough is unlikely.

9. Application Verification

Application verification samples collectors were placed within test plots prior to application (pp. 13, 34). The collectors were 150 mm petri dishes fitted with 150 mm filter paper trimmed to fit inside the petri dishes. Fifteen sample collectors were placed in each test plot in a line across the plot perpendicular to the direction of application. Petri dish covers were removed immediately prior to application and replaced immediately afterward. All application verification samples were placed in plastic bags and packed in coolers until transport to the lab for analysis (p. 37).

Petri dish samples were composites of the 15 petri dishes per field site (p. 134). The total residue found in the composite sample for Site 1W was 20,013 µg and for Site 2E was 22,825 µg. Reviewer calculated recoveries for the two sites were 67% and 77%, respectively (theoretical amount of a.i. per petri dish (p. 153) 1,983.3 µg × 15 petri dishes = 29,750 µg per composite sample).

Mean procedural recoveries of dicamba on petri dish samples was 97% (pp. 14, 123).

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

Flux modeling was determined using the aerodynamic method following the Thornthwaite-Holzman aerodynamic flux equation and by the indirect method following the CDPR methodology (p. 18; Appendix C, pp. 214-226).

Aerodynamic Method

The aerodynamic method, also referred to as the "flux-gradient" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., *1990.*

The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation, which is shown in the following expression:

$$\text{Equation } x_1 \qquad P = \frac{k^2(\Delta\bar{c})(\Delta\bar{u})}{\phi_m\phi_p[\ln\left(\dfrac{z_2}{z_1}\right)]^2}$$

where P is the flux in units of $\mu g/m^2 \cdot s$, k is the von Karman's constant (dimensionless ~0.4), $\Delta\bar{c}$ is the vertical gradient pesticide residue concentration in air in units of $\mu g/m^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta\bar{u}$ is the vertical gradient wind speed in units of m/s between heights z_{top} and z_{bottom}, and ϕ_m and ϕ_p are the momentum and vapor stability correction terms respectively. Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into Equation 2-1 to arrive at Equation 2-2 which is ultimately used to compute the flux.

$$\text{Equation } x_2 \qquad Flux = \frac{-(0.42)^2(c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m\phi_p\ln\left(\dfrac{z_{top}}{z_{bottom}}\right)^2}$$

where ϕ_m and ϕ_p are internal boundary layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

$$\text{Equation } x_3 \qquad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\dfrac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + (u_{ztop} - u_{zbottom})^2}$$

where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if $R_i > 0$ (for Stagnant/Stable IBL)
$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)
$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid [was/was not] satisfied at all times [List the sampling periods and resulting fetches with exceptions]. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

Indirect Method

The indirect method, commonly referred to as the "back calculation" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information are used in combination with the ISCST3 dispersion model (Version 02035) and a unit flux rate of 0.001 $\mu g/m^2 \cdot s$ to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the ISC model runs are compared to those concentrations actually measured, and a regression is performed, using the modeled values along the x-axis and the measured values along the y-axis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson et al., 1999.

B. Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Tables 5** and **6**.

Table 5. Field volatilization flux rates of dicamba obtained in study [Site 1W]

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			Notes
			Reviewer (μg/m^2-sec)	Registrant (μg/m^2-sec)	Empirical Flux Determination Method	
1	04/11/16 9:32 – 12:51	3.32		0.0016 0.0056	AD ID	
2	04/11/16 12:51 – 15:50	2.98		0.0022 0.011	AD ID	
3	04/11/16 15:50 – 20:59	5.15		0.0012 0.0015 & 0.0021	AD ID	
4	04/11/16 20:59 – 04/12/168: 59	12.00		0.000054 0.00051	AD ID	
5	04/12/16 8:59 - 20:44	11.75				
6	04/12/16 20:44 – 04/13/16 8:32	11.80				

Data obtained from Table 1, p. 218; Table 9, p. 223; and Table 11, p. 226 in the study report.
*Methods legend: AD = Aerodynamic Method, ID = Indirect Method.
Dicamba was not detected sufficiently frequently to determine flux estimates during sampling periods 5 and 6.

Table 6. Field volatilization flux rates of dicamba obtained in study [Site 2E]

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			Notes
			Reviewer ($\mu g/m^2$-sec)	Registrant ($\mu g/m^2$-sec)	Empirical Flux Determination Method	
1	04/11/16 10:35 – 13:46	3.18		0.0014	AD	
2	04/11/16 13:46 – 16:40	2.90		0.0011	AD	
3	04/11/16 16:40 – 21:24	4.73		0.00038 0.00099	AD ID	
4	04/11/16 21:24 – 04/12/16 10:33	13.15		0.00017	AD	
5	04/12/16 10:33 - 21:43	11.17				
6	04/12/16 21:43 – 04/13/16 9:08	11.42				

Data obtained from Table 2, p. 219; Table 10, p. 224; and Table 11, p. 226 in the study report.
*Methods legend: AD = Aerodynamic Method, ID = Indirect Method.
Dicamba was not detected sufficiently frequently to determine flux estimates during sampling periods 5 and 6.

Maximum volatile flux rates occurred during sampling periods 1 or 2 shortly after application. Dicamba was not detected above the LOQ during sampling periods 5 and 6; hence, the flux was not estimated for these periods.

Regression coefficients relating concentration, wind speed, and temperature to height were statistically significant for all regressions, though the correlation coefficients varied (p. 220). For Site 1W, the r^2 values for concentration were >0.9 for the first and fourth sampling periods, but 0.49 and 0.59 for the second and third sampling periods. For wind speed, the r^2 for the regressions were >0.9 for the first and second periods, but only 0.37 and 0.41 for third and fourth periods, likely due to low wind speeds near the anemometer detection limits. For temperatures, all r^2 values were >0.87.

For Site 2E, the r^2 values for concentration and height were 0.81 or higher; however, there were more values below the LOQ or LOD for Site 2E than for Site 1W. For wind speed, the regressions for Site 2E were 0.98 or greater and for temperatures were 0.91 or greater (p. 221).

Limited quantified residues at offsite monitors significantly limited the analysis using the indirect method. There were six detects above the LOQ at Site 1W and only one detect at Site

2E. A simplified approach was used where the flux was estimated as the ratio of the measured air concentration and predicted air concentration multiplied by the nominal flux of 10^{-6} g/m^2-sec (pp. 225-226).

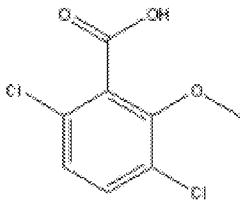## III. Study Deficiencies and Reviewer's Comments

1. The estimated flux values in Tables 9 and 10 (pp. 223-224) were not calculated correctly from the regressed values, Richardson Number, and Internal Boundary Layer stability correction terms provided in those tables. The reviewer notes that it appears possible that incorrect heights were used in the calculation.

2. Based on reviewer calculations, the application verification samples contained only 67% and 77% of the targeted amount of dicamba applied at Sites 1W and 2E, respectively.

3. Reviewer calculated average meteorological parameters do not agree with the reported values for all sampling heights. Reviewer calculated average wind speeds at 1 m (reported as 55 cm in Table 4, p. 22) for the 0-3 hr and 6-12 hr sampling periods are 2.40 m/s and 1.64 m/s, as opposed to 2.20 m/s and 2.40 m/s, respectively. Similarly average temperature data do not agree for all sampling periods.

4. The soil matrix was not sampled. Soil bulk density, soil temperature, soil moisture, and organic matter content were not reported.

5. The minimum fetch required for use of the aerodynamic method was not satisfied for the samplers positioned at 0.8 and 1.0 meters above the hay.

6. A control sample was collected upwind of each site, but no untreated replicate subplot was established.

7. Air samples were only collected through 48 hours instead of the targeted 72 hours due to forecast air temperatures that were lower than the target temperature (p. 38).

8. Field spiked samples were not deployed.

9. No independent analytical method validation was performed. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.

10. Storage stability of the test material was not provided. Information about the stability of dicamba residues on the sampling matrix was provided.

11. The initial air monitoring period did not start at the beginning of the application period, but instead started immediately following the application period.

12. No pre-application samples were collected.

13. The test plot was not irrigated. The study design should include irrigation according to the label requirements.

14. The heights at which meteorological data were collected are incorrect in Tables 4, 5, 7, and 8 (pp. 220-222). The correct heights should be 50 cm, 100 cm, and 150 cm instead of 33 cm, 55 cm, and 90 cm.

15. Wind speed and temperature measurements were reported in units of mph and °F instead of m/s and °C.

IV. References

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. Environmental Science and Technology, 24:1490-1497.

Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

Attachment 1: Chemical Names and Structures

Code Name/ Synonym	Chemical Name	Chemical Structure
PARENT		
Engenia® Herbicide/ Dicamba as the BAPMA salt	**IUPAC:** 3,6-Dichloro-*o*-anisic acid, BAPMA salt **CAS:** 3,6-Dichloro-2-methoxybenzoic acid, BAPMA salt **CAS No.:** 104040-79-1 **Formula:** $C_8H_6Cl_2O_3$ **MW:** 221.04 g/mol **SMILES String:** CLc1ccc(CL)c(OC)c1C(=O)(O)	

Attachment 2: Statistics Spreadsheets and Graphs

[Insert supporting electronic spreadsheet files here (electronic attachment files are electronically finalized as separate files as well). Name electronic attachments the same file name as the Microsoft Word study review file with the addition of "Calc" for Excel workbooks and WinZip files, the addition of "Data" for Adobe Acrobat and Document Imaging files, and the addition of brief descriptors as appropriate for SigmaPlot Notebooks. Compress electronic attachment files into a WinZip file when three or more are prepared for a study review.]

[Print hard copies of the study review and any attachment sheets from separate electronic files to produce one hard copy file for finalization.]

[Example Excel files and spreadsheets follow below.]

1. Validation spreadsheet for studies following the Indirect Method:

Indirect Method.xlsx

2. Validation spreadsheet for studies following the Aerodynamic Method:

Aerodynamic
Method.xlsx

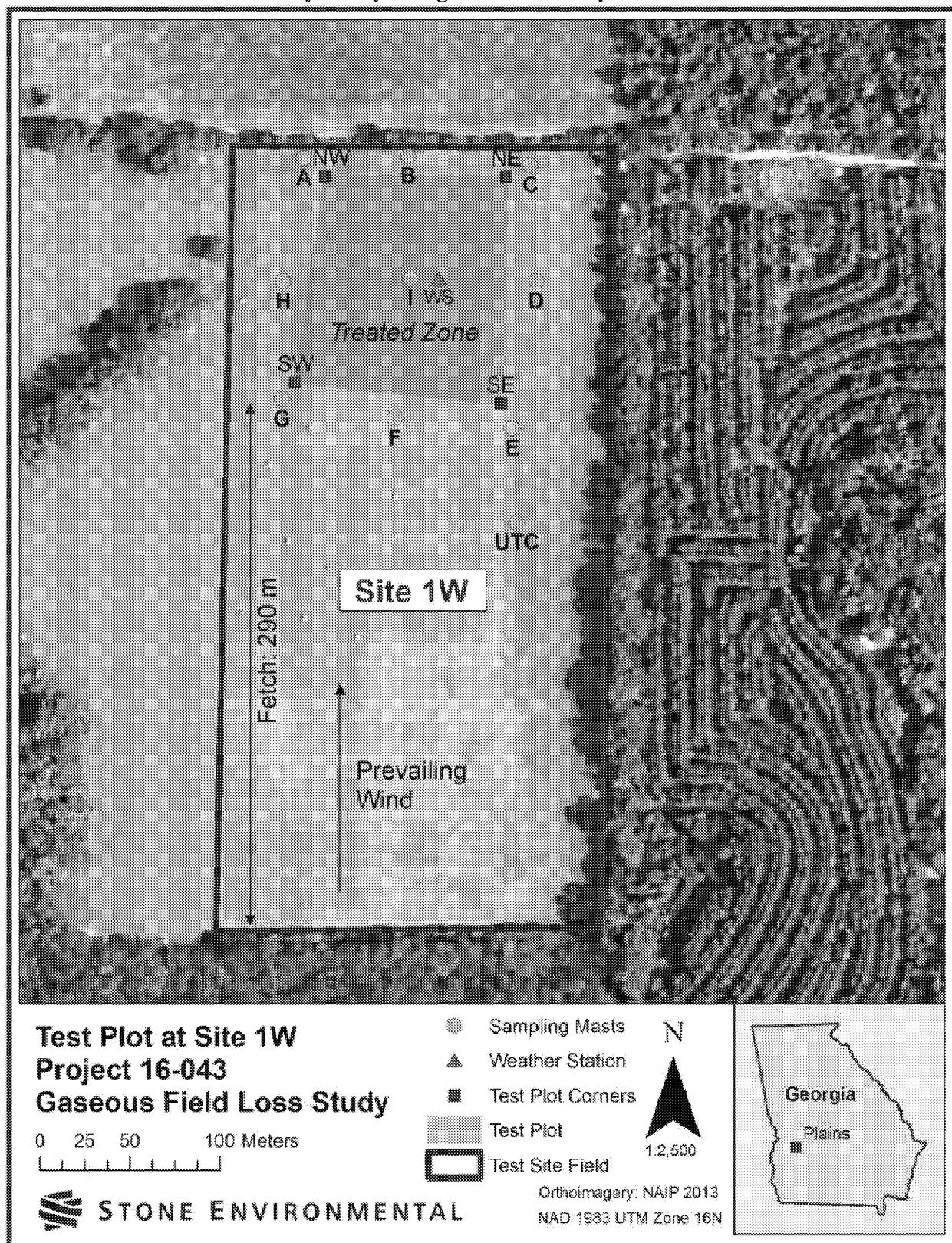**Attachment 3: Field Volatility Study Design and Plot Maps**

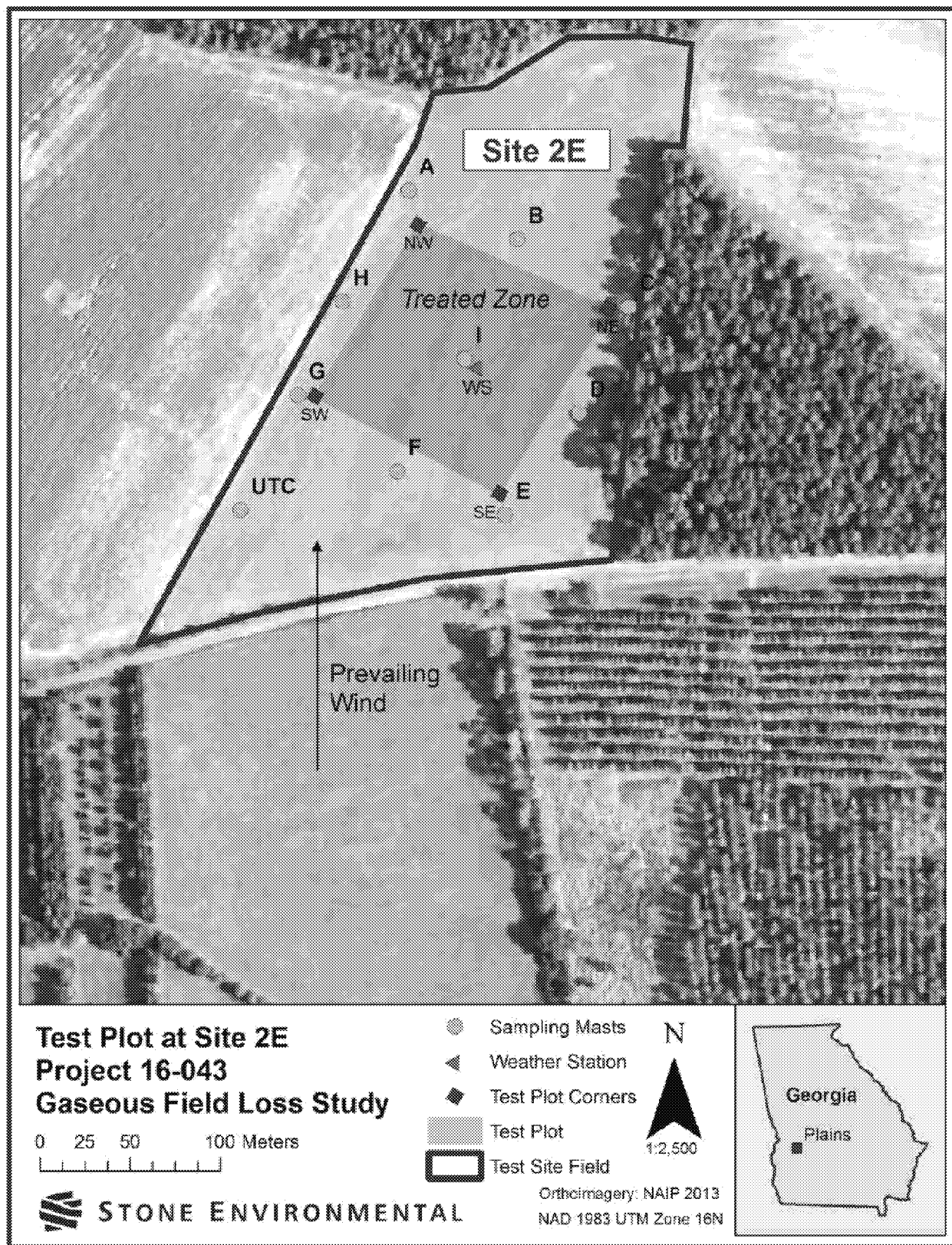Figure obtained from Figure 2, p. 43 of the study report.

Test Plot at Site 2E
Project 16-043
Gaseous Field Loss Study

0   25   50   100 Meters

STONE ENVIRONMENTAL

Figure obtained from Figure 3, p. 44 of the study report.

Attachment 4: Calculations and Index of Variables Used in Flux Determination Methods

Aerodynamic Method

$$\text{Equation x}_1 \quad Flux = \frac{-(0.42)^2 (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\dfrac{z_{top}}{z_{bottom}}\right)^2}$$

Flux ($\mu g/m^2 s$): volatile flux of pesticide from release source surface

c_{ztop} ($\mu g/m^3$): concentration at the top sampler adjusted according to the regression of concentration vs. ln (height)

$c_{zbottom}$ ($\mu g/m^3$): concentration at the bottom sampler adjusted according to the regression of concentration vs. ln (height)

u_{ztop} (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

$u_{zbottom}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

ϕ_m and ϕ_p (dimensionless): Internal Boundary Layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

$$\text{Equation x}_2 \quad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\dfrac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + \left(u_{ztop} - u_{zbottom}\right)^2}$$

where:

T_{ztop}: Temperature at the top sampler adjusted according to the regression of temperature vs. ln (height)

$T_{zbottom}$: Temperature at the bottom sampler adjusted according to the regression of temperature vs. ln (height)

R_i (dimensionless): Richardson Number

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = \left(1 + 16R_i\right)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = \left(1 - 16R_i\right)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$